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Effect of Ni addition on the glass-forming ability and soft-magnetic properties of FeNiBPNb metallic glasses

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The effect of Ni addition on the glass-forming ability (GFA) and soft-magnetic properties of an $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ (x=0–0.6) alloy system were investigated. We found that the addition of Ni was effective in allowing the alloy to approach a eutectic point as well as increasing the thermal stability of the supercooled liquid. By increasing the amount of Ni, the supercooled liquid region (ΔT_x), the reduced glass transition temperature T_{rg} (T_g/T_l) and the γ parameter [$T_x/(T_g+T_l)$] increased from 49 to 75 K, 0.540 to 0.594 and 0.373 to 0.405, respectively. As a result, novel $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ bulk metallic glass (BMG) rods with a maximum diameter of 1 mm were synthesized with a composition of x=0.5 and x=0.6 by copper mold casting. These metallic glasses have a moderate saturation magnetization of 0.37–1.20 T with good soft-magnetic properties, i.e. a low coercivity of 1.4–3.3 A/m and a high effective permeability of 13100–20900 at 1 kHz. The simultaneous achievement of a high GFA and good soft-magnetic properties for the FeNi-based alloy system is promising for the future development of BMGs.

FeNi-based metallic glass, glass-forming ability, soft-magnetic properties

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Fe-based bulk metallic glasses (BMGs) have attracted an increasing amount of attention because of their excellent soft-magnetic properties, high fracture strength, high hardness and good corrosion resistance. Since the first synthesis of an Fe-based ferromagnetic BMG with a wide supercooled liquid region in a Fe-(Al, Ga)-metalloid system in 1995 [1,2], much effort has been devoted to the search for BMG systems with high glass-forming ability (GFA) and good soft-magnetic properties. A variety of Fe-based BMGs have been developed for potential application as functional and structural materials such as FePC-based BMGs, FeBSi-based BMGs and their extensive derivatives [3–6]. Consequently, a breakthrough in the development of novel Fe-based BMG is of primary importance and the search for new systems with good soft-magnetic properties has always been a hot issue. Recently, a new $Fe_{77}B_{13}P_7Nb_3$ metallic glass system with a wide ΔT_x and low core loss has been developed at the NEC Tokin Corporation, Japan [7]. However, because of its low glassy-forming ability, only ribbons with thicknesses of 100–120 μm were prepared. In addition, it has disadvantages of a relatively high coercivity (H_c) of more than 2 A/m, low effective permeability (μ_e) and poor μ_e stability upon an increase in frequency. Nevertheless, this system is promising for the development of a novel BMG because of the significant difference in atomic size and the large negative heats of mixing between the elements.

In this study, we aimed to develop an FePBNb metallic glass system with a much higher GFA and good soft-magnetic properties by examining the effect of Ni addition on the GFA and the soft-magnetic properties based on two factors: (1) As a ferromagnetic element, Ni has been shown to be effective in improving the soft-magnetic properties in

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permalloys and FeNi-base metallic glasses [5,8,9]. (2) Ni shows mutual solubility with Fe and has been shown to be effective in improving the thermal stability of the supercooled liquid as well as allowing the alloy to approach a eutectic point composition leading to a high GFA [10–12]. As a result, Fe-based BMGs with a diameter of 1 mm and good soft-magnetic properties in $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ alloys with x=0.5 and x=0.6 were successfully synthesized.

1 Experiment methods

Multicomponent alloy ingots with nominal compositions of $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) were premelted by induction-melting mixtures of pure Fe (99.99 mass%), Ni (99.9 mass%), Nb (99.9 mass%), B (99.5 mass%) and pre-alloyed Fe-P ingots under a high-purity argon atmosphere. Metallic glass ribbons with thicknesses of about 20 μm and a width of 1 mm were prepared by the single copper roller melt-spinning method. Cylindrical alloy rods with diameters up to 2 mm were produced by copper mold casting in an argon atmosphere. The glassy structure was identified by X-ray diffraction (XRD; D8, Bruker, Germany) with Cu Kα radiation. Thermal stability associated with the glass transition temperature (T_g), crystallization temperature (T_x), and supercooled liquid region ($\Delta T_x=T_x-T_g$) was examined by differential scanning calorimetry (DSC; 404C, Netzsch, Germany) at a heating rate of 0.67 K/s. The liquidus temperature (T_l) was measured using a DSC by cooling the molten alloy samples at a cooling rate of 0.067 K/s. The magnetic properties of the saturation magnetization (I_s) under a maximum applied field of 800 kA/m were measured with a vibrating sample magnetometer (VSM; 7410, Lake Shore, USA). H_c was measured with a B-H loop tracer (BHS-40, Riken, Japan) under a field of 1000 A/m. μ_e at 1 kHz was measured with an impedance analyzer (4294A, Agilent, USA) under a field of 1 A/m. All the ribbon samples for magnetic property measurements were annealed at T_g−50 K for 600 s to improve the soft-magnetic properties through structural relaxation.

2 Results and discussion

The X-ray diffraction patterns confirmed that all the melt-spun ribbons used for thermal and magnetic tests are composed of a full glassy phase without crystallization. Figure 1 (a) shows DSC curves of the melt-spun $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) metallic glasses. The alloys exhibit a glass transition followed by a large supercooled liquid region and then crystallization. T_g and T_x decrease gradually from 788 to 714 K and from 837 to 777 K, respectively, with an increase in the Ni content from x=0 to x=0.6. Additionally, the ΔT_x increases remarkably from 49 to 75 K with an increase in the Ni content to x=0.5, and

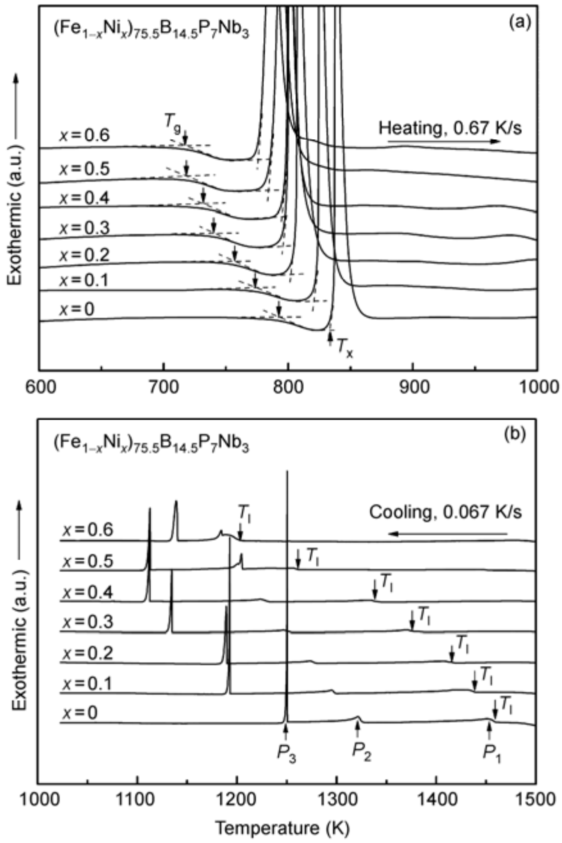

Figure 1 DSC curves for the $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) glassy alloys (a) and the master alloys (b).

then decreases to 63 K when x=0.6. Thus, the thermal stability of the supercooled liquid effectively increases with an increase in the Ni content to x=0.5, and it decreases with a further increase in Ni content.

Figure 1 (b) shows DSC curves of the $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) alloys and the cooling behavior of this metallic glass system is obvious. It is clearly seen that T_l decreases drastically from 1459 to 1203 K with an increase in Ni content, and the temperature interval between the three exothermic peaks marked with P_1, P_2 and P_3 decreases gradually with an increase in Ni content. The P_1 and P_2 exothermic peaks of the alloy with x=0.6 almost overlap indicating that the alloy approaches a eutectic point. Accordingly, the reduced glass transition temperature T_{rg} (T_g/T_l) and γ parameter $[T_x/(T_g+T_l)]$ decrease slightly first and then increase markedly from 0.540 to 0.594 and from 0.373 to 0.405, respectively. All these changes imply that the addition of Ni was effective in bringing the alloy composition close to a eutectic point in this alloy system.

Based on the results of the DSC measurement and the thermal stability analyses, we expect the GFA of this alloy system to be effectively enhanced. Therefore, we tried to prepare cylindrical metallic glass rods for the $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) alloys. All the cast alloy rods with diameters of 1 mm were characterized by XRD using Cu Kα radiation. In agreement with the thermal analyses for compositions with x=0.5 and x=0.6, the XRD patterns only contained broad peaks without crystalline peaks indicating the formation of a glassy phase. Their as-cast surfaces all appeared smooth and lustrous. No apparent volume reduction was recognized on their surfaces indicating that there was no drastic crystallization during the formation of these samples. On the contrary, for alloys with x=0.4, an apparent crystallization with the $Fe_3P_{0.37}B_{0.63}$, $(Fe,Ni)_{23}B_6$ and FeB phases was evident. Figure 2 shows a DSC curve of the as-cast $(Fe_{0.5}Ni_{0.5})_{75.5}B_{14.5}P_7Nb_3$ alloy rod with a diameter of 1 mm together with the DSC curve of the melt-spun metallic glass ribbon for comparison. No appreciable differences in T_g, T_x, ΔT_x or the crystallization process were observed between the melt-spun ribbon and the rod samples. The XRD and DSC measurement results clearly indicate the preparation of a $(Fe_{0.5}Ni_{0.5})_{75.5}B_{14.5}P_7Nb_3$ BMG with a diameter of 1 mm. Here we want to emphasize that such an Fe-based ferromagnetic BMG has never been successfully prepared to date.

Figure 3 shows hysteresis I–H loops of melt-spun $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) metallic glasses. The I_s decreases monotonically from 1.2 to 0.37 T upon increasing the Ni content from x=0 to x=0.6, and this can be attributed to the lower magnetic moment of Ni (0.6 μ_B) compared with that of Fe (2.2 μ_B). With an increase in the Ni content from x=0.1 to x=0.6, the H_c decreases from 3.3 to 1.4 A/m. As shown in the inset of Figure 3, the alloys with x=0.5 and x=0.6 exhibit a typical soft-magnetic hysteresis with low coercive forces of 1.7 and 1.4 A/m. The reason for this is the significant increase in the GFA, which leads to a high degree of amorphicity and structural homogeneity resulting in a decrease in the magnetocrystalline anisotropies [13]. The frequency dependence of the permeability under a field of 1 A/m is shown in Figure 4 and the μ_e at 1 kHz increases from about 13100 to

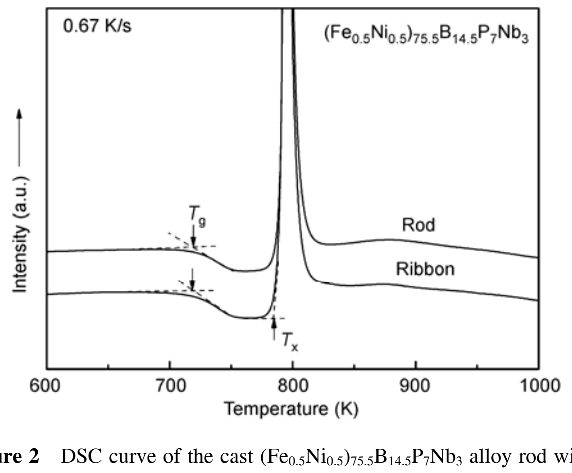

Figure 2 DSC curve of the cast $(Fe_{0.5}Ni_{0.5})_{75.5}B_{14.5}P_7Nb_3$ alloy rod with a diameter of 1 mm together with a DSC curve of the melt-spun metallic glass ribbon for comparison.

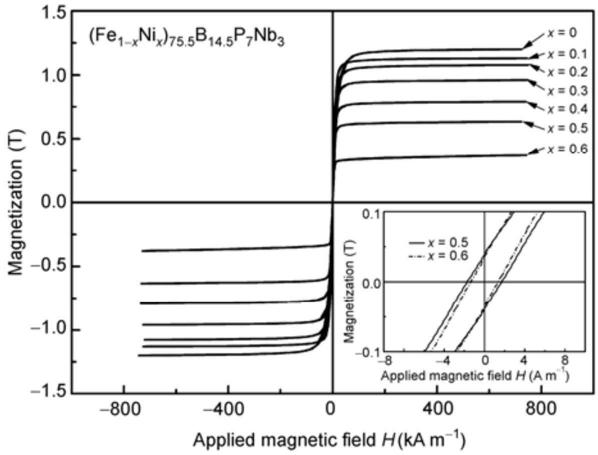

Figure 3 Hysteresis I–H loops of melt-spun $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) metallic glasses. The inset shows B–H hysteresis loops of the metallic glasses with x=0.5 and x=0.6.

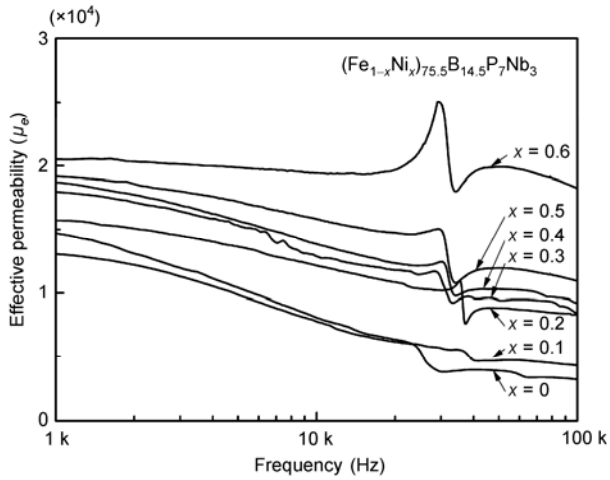

Figure 4 Effective permeability as a function of applied field frequency for the $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) melt-spun metallic glass ribbons annealed for 600 s at T_g–50 K.

20900 with an increase in the Ni content, and this is in agreement with the high GFA and the low H_c. Ni addition is very effective in enhancing the stability of μ_e upon an increase in frequency. As shown in the Figure 4, for the alloy with x=0.5 and x=0.6, μ_e remains as high as 15800 and 19400 when the frequency is increased to 10 kHz. Even at 20 kHz, which is just below the cut-off frequency, μ_e remains high at 14800 and 19500, respectively. The μ_e of the alloys with a Ni content less than x=0.4 decreases rapidly with an increase in the frequency. Table 1 summarizes the thermal parameters and magnetic properties of the $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) metallic glasses. In addition to the enhancement of the GFA, the soft-magnetic properties also improve upon the addition of Ni.

Based on the above results, we can explore the origin of the enhanced GFA as a result of Ni addition in the FeBPNb

Table 1 Thermal parameters and magnetic properties of the as-spun $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) metallic glasses

Composition (at%)	Thermal parameters						Magnetic properties		
	T_g (K)	T_x (K)	ΔT_x (K)	T_l (K)	T_{rg}	γ	I_s (T)	H_c (Am^{-1})	μ_e
$Fe_{75.5}B_{14.5}P_7Nb_3$	788	837	49	1459	0.540	0.373	1.20	3.3	13100
$(Fe_{0.9}Ni_{0.1})_{75.5}B_{14.5}P_7Nb_3$	770	824	54	1438	0.535	0.373	1.13	2.8	14700
$(Fe_{0.8}Ni_{0.2})_{75.5}B_{14.5}P_7Nb_3$	749	807	58	1415	0.529	0.373	1.07	2.7	15700
$(Fe_{0.7}Ni_{0.3})_{75.5}B_{14.5}P_7Nb_3$	737	800	63	1376	0.536	0.379	0.96	2.5	16300
$(Fe_{0.6}Ni_{0.4})_{75.5}B_{14.5}P_7Nb_3$	726	799	73	1339	0.542	0.387	0.79	2.3	17900
$(Fe_{0.5}Ni_{0.5})_{75.5}B_{14.5}P_7Nb_3$	715	790	75	1261	0.568	0.400	0.64	1.7	19200
$(Fe_{0.4}Ni_{0.6})_{75.5}B_{14.5}P_7Nb_3$	714	777	63	1203	0.594	0.405	0.37	1.4	20900

metallic glasses as follows. First, we consider the effect of atom size on the glass forming ability [14]. The constituent elements have a large atomic size mismatch except for the similar elements Fe and Ni. The atomic radius changes in the following order: Nb>Fe(Ni)>P>B. The mismatch between Nb-Fe(Ni), Fe(Ni)-P and P-B are 15.3%, 13.8% and 21.1%, respectively. The large (L) and small atoms (S) may form a strong L-S percolating network or reinforced "backbone" structure in the amorphous structure [15] resulting in an enhancement of the stability of the undercooled liquid and this further suppresses crystallization [16]. In addition, the elements have large negative heats of mixing, i.e. –31 kJ/mol for Fe-P, –16 kJ/mol for Fe-Nb, –11 kJ/mol for Fe-B, –30 kJ/mol for Ni-Nb, –26 kJ/mol for Ni-P, –39 kJ/mol for B-Nb and –81 kJ/mol for P-Nb [17]. It has been previously reported that metallic glasses that conform to the component rules can have a unique glassy structure with a higher degree of dense and randomly packed atomic configurations, new local atomic configurations and long-range attractive interactions [15,18,19]. In an alloy liquid with these structural features, atomic redistribution is restrained leading to an increase in viscosity as well as a suppression of the atomic rearrangement, which would progress the crystallization reaction.

The second reason considered here is based on the finding that the addition of Ni was effective in increasing the stability of the supercooled liquid as well as allowing the alloys to approach a eutectic point. ΔT_x increases from 49 to 75 K with an increase in the Ni content to 0.5, as shown in Table 1. This means that the supercooled liquid is much more stable and the precipitation of the crystalline phases is suppressed [20]. The addition of Ni effectively allows the alloy to approach a eutectic point, as shown in Figure 1 (b), resulting in an increase of the reduced glass transition temperature T_{rg} and the γ parameter from 0.540 to 0.594 and 0.373 to 0.405, respectively, as shown in Table 1. The precipitation of a crystalline phase is kinetically unfavorable for long-range atomic diffusion [21].

The third reason has been given by studies [22,23] which stated that the appropriate substitution of similar atoms can significantly improve the glass forming ability by decreasing the difference in energy between the solid glass and its liquid state ΔG (G^s–G^l), which reflects the stability of the glassy state [24]. Because Fe and Ni both belong to group VIIIA in the Periodic Table of the Elements (PTE), the difference in atomic size between Fe (0.124 nm) and Ni (0.125 nm) is negligible and their physical and chemical properties are also quite similar. Fe and Ni show a mutual solubility below the liquidus temperature. The addition of Ni to the $(Fe_{1-x}Ni_x)_{75.5}B_{14.5}P_7Nb_3$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) alloy system may increase the complexity of crystallization for a transformation from the metastable undercooled liquid state to a completely crystalline compound during the heating process [25,26].

3 Conclusions

The effect of Ni addition on the glass forming ability and soft-magnetic properties of a FeBPNb alloy were investigated with the aim of synthesizing a novel FeNiBPNb BMG. As a result, the glass forming ability distinctly improved because of the stabilization of the supercooled liquid and the fact that the alloy approached a eutectic point upon Ni addition. BMG rods with a maximum diameter of 1 mm were formed by the addition. Accompanied with a high glass forming ability as well as having good soft-magnetic properties at a low H_c of 1.4–1.7 A/m and a high μ_e of 19200–20900, the FeNiBPNb system BMGs are important for the future development of new Fe-based soft-magnetic BMGs.

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